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Spent fuel reprocessing based on electrochemical extraction process (SREEP)

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Abstract

A new concept of the electrochemical process for the reprocessing of nuclear spent fuel, SREEP, has been developed on the basis of fundamental studies of the electrochemical reactions of actinide elements and fission products. SREEP consists of unit processes for (1) spent fuel dissolution by electrolytic oxidation, (2) recovery of platinum group metals by electrodeposition, (3) TBP extraction of U, Pu and Np after the successive electrolytic preparation of U(VI), Pu(IV) and Np(VI), (4) recovery of Cs and Sr by electrolytic ion transfer extraction and (5) separation of transplutonium and lanthanide elements by electrodeposition in the molten salt.

1. Introduction

Many studies have been performed [1–3] for the improvement of the currently employed spent fuel reprocessing processes such as the Purex process and for the development of novel reprocessing techniques in order to meet the requirements of advanced nuclear technology. Recent advances are the utilization of plutonium as U–Pu mixed oxide in a power reactor and the efficient burning of the fuel up to higher burn-up. In designing an advanced reprocessing process, the following requisites should be taken into account: (i) improvement in the partitioning efficiency of uranium, transuranium and fission products; (ii) minimization of the amount of radioactive waste; (iii) reduction of construction and/or operation costs; and so forth.

The electrochemical procedure exhibits many essential advantages in that the amount of chemical waste can be minimized and the process can be operated automatically and remotely. Application of the electrochemical procedure to nuclear technology such as the reprocessing process, however, is so far very limited [1]. In the present paper a new concept of spent fuel reprocessing based on the electrochemical extraction process, SREEP, is proposed.

2. Recommended process flow of SREEP

The process flow of SREEP is shown in Fig. 1.

3. Results and discussion

3.1. *Spent fuel dissolution by electrolytic oxidation (DEO)*

Decladded spent fuel is dissolved in nitric acid solution containing Ce(IV) [4–6]. The dissolution of a refractory oxide such as PuO_2 is enhanced by the presence of the strong oxidant and a rapid and complete dissolution of the spent fuel can be attained. The oxidant Ce(IV) is regenerated by galvanostatic electrolysis using a platinum gauze anode placed in the dissolving solution. The oxidation states of U, Np and Pu in the effluent solution from the DEO process are U(VI), Np(VI) and Pu(VI).

3.2. *Recovery of platinum group metals by electrodeposition (PED)*

Platinum group metals are recovered by electroreduction and deposition using a flow-through electrode. A column electrode of glassy carbon (GC) fibres as the working electrode is employed [7] to study the electrodeposition behaviour of metals. Using a column electrode with an extremely large surface area, one can perform quantitative and rapid electrolysis with flowing of the sample solution through the column. Complete recovery of Pd and Rh is attained by controlled potential electrolysis at a more negative potential than 0.3 V *vs.* Ag–AgCl/saturated KCl (SSE) and at a more negative potential than 0.0 V respectively. RuO_4 generated in the DEO process can also be reduced and recovered in the PED process as an insoluble RuO_2 deposit. When the electrolysis potential employed for

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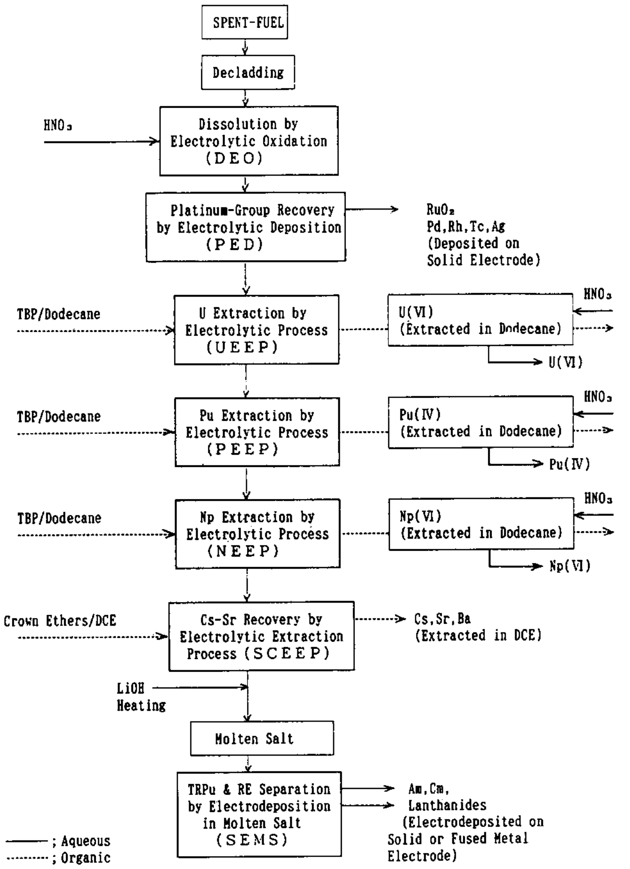

Fig. 1. Process flow of SREEP.

the PED process is −0.05 V, the oxidation states of U, Np and Pu in the effluent from PED are U(IV) with a small quantity of U(VI), Np(V) and Pu(III) [7, 8].

3.3. Electrolytic extraction of U, Pu and Np (UEEP, PEEP and NEEP)

The oxidation states of U, Pu and Np ions are precisely controlled by the controlled potential electrolysis and then separated by conventional TBP/dodecane extraction. Here the flow-through column electrode as described above is used for the electrolytic preparation of U, Pu and Np ions. On the basis of current–potential curves [7, 8] for the reduction and oxidation of U, Np and Pu in various oxidation states, recorded by flow coulometry with a multistep column electrode system, appropriate conditions for the preparation of ions in desired oxidation states can be established. In SREEP, TBP extraction of U(VI), Pu(IV) and Np(VI) is adopted for partitioning these elements.

The nitric acid effluent (2–3 M HNO_3 solution) from the PED process, containing U(IV)+U(VI), Np(V) and Pu(III) is electrolysed at the flow-through electrode at 0.50 V, where U(IV) is oxidized into U(VI) but Pu(III) and Np(V) are not electrolysed. Then U(VI) is extracted into TBP/dodecane (UEEP). The effluent from UEEP is introduced into PEEP consisting of the flow-through electrode at 0.80 V, where Pu(III) is quantitatively oxidized into extractable Pu(IV). The oxidation of Np(V) does not take place at 0.80 V. In the succeeding step (NEEP) Np(V) is converted to extractable Np(VI) at the flow-through electrode at 1.30 V.

3.4. Recovery of Cs and Sr by electrolytic ion transfer extraction (SCEEP)

Alkali and alkaline earth metal ions such as Cs^+ and Sr^{2+} are transferred electrolytically across the interface between the aqueous solution and an organic solvent such as 1,2-dichloroethane or nitrobenzene [9]. By applying sufficient interfacial potential for the objective ion to transfer from the aqueous to the organic phase, the ion can be extracted into organic solution by controlled potential electrolysis. The ion transfer is facilitated by the presence of an ionophore such as a crown ether which complexes strongly and selectively with alkali and alkaline earth metal ions. The addition of a suitable ionophore to the organic phase may improve the efficiency as well as the selectivity of the separation. The electrolytic ion transfer extraction has the distinct advantage that it is not required to add a counter-anion, which is indispensable in conventional ion pair solvent extraction.

3.5. Separation of transplutonium and lanthanide elements by electrodeposition in molten salt (SEMS)

Am, Cm and lanthanide elements are recovered at the solid electrode by electrolytic reduction in a molten salt such as an alkali chloride or nitrate. In this connection many studies have been performed to develop a pyrometallurgical partitioning process based on the recovery of metals by electrodeposition in molten KCl–LiCl eutectic salt [3, 10, 11]. Efficient partitioning of uranium, plutonium, neptunium, Cs and Sr, platinum group metals, trivalent transplutonium and lanthanides from spent fuel can be achieved by SREEP utilizing various electrochemical reactions. The advantage of the electrochemical method in making precise control of the electrolytic potential possible results in an enhancement of the selectivity in the separation. The amount of radioactive waste can be minimized, since the electrochemical method essentially requires no chemicals to be added. It is also advantageous that the electrochemical operation can be remotely controlled by fairly simple devices.

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